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(19) (CA) **CANADIAN PATENT** (12)

(54) Molecule-Based Microelectronic Devices

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ABSTRACT OF THE DISCLOSURE

1 Several types of new microelectronic devices
including diodes, transistors, sensors, surface energy
storage elements, and light-emitting devices are
disclosed. The properties of these devices can be
5 controlled by molecular-level changes in electroactive
polymer components. These polymer components are formed
from electrochemically polymerizable material whose
physical properties change in response to chemical
changes, and can be used to bring about an electrical
10 connection between two or more closely spaced
microelectrodes. Examples of such materials include
polypyrrole, polyaniline, and polythiophene, which respond
to changes in redox potential. Each electrode can be
individually addressed and characterized electrochemically
15 by controlling the amount and chemical composition of the
functionalizing polymer. Sensitivity of the devices may
be increased by decreasing separation between electrodes
as well as altering the chemical environment of the
electrode-confined polymer. These very small, specific,
20 sensitive devices provide means for interfacing electrical
and chemical systems while consuming very little power.

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This application is a division of application
serial number 495,996 filed November 22, 1985.

5

Background of the Invention

Presently available solid state microelectronic devices consist of microcircuits with discrete circuit elements such as monolithic integrated circuits, transistors, diodes, resistors, capacitors, transformers, and conductors mounted on an insulating substrate. Thin film hybrid microcircuits are formed by vapor deposition of conductors, such as copper and gold, and resistors, such as tantalum, nichrome, and tin oxide onto a passive or insulating substrate such as silicon dioxide. An exact conductor pattern is obtained by masking or photolithographic etching. The entire circuit is subsequently encased with an epoxy dip to protect against moisture and contamination.

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Modern integrated circuit devices, even highly miniaturized very large scale integrated devices (VLSI), are responsive only to electrical signals. There is now considerable interest in interfacing microelectronic devices with chemical and biological systems and it is therefore highly desirable to provide a microelectronic device that is responsive to such chemical or biological inputs. Typical applications for these devices include



1 sensing of changes in pH and molar concentrations of chemical compounds, oxygen, hydrogen, and enzyme substrate concentrations.

5 Applicant is not aware of any apparatus or system which allows a direct interface between a microelectronic device sensitive to chemical inputs and a microminiature electrical circuit. Devices have been made on a larger scale which are sensitive to chemical input. These devices include such well known apparatus as pH 10 sensors. Work in this area has recently centered around the use of electroactive polymers, such as polypyrrole or polythiophene. These compounds change conductivity in response to changes in redox potential. Recently, a polymeric semiconductor field effect transistor has been 15 disclosed in a Japanese patent, 58-114465. As described in this patent, polymers such as trans-polyacetylene, cis-polyacetylene, polypyrrole, and polyvinyl phenylene have been used as inexpensive substitutes for single crystal silicon or germanium in making a semiconductor field effect transistor. There is no recognition of the unique 20 properties of these polymers in this patent and, in fact, the polymers are treated as semiconducting material even though the properties of the polymers are distinctly different from that of silicon or germanium. The polymers 25 are used as substitutes for semiconducting materials

1 sensitive to electrical signals for uses such as in memory
storage. Disadvantages to the FET as disclosed are that
it is unstable and has a short useful life.

5 It is therefore an object of the present
invention to provide a process for producing
microelectronic devices responsive to chemical input which
can be incorporated into microelectronic systems which are
responsive to electrical input.

10 A further object of the present invention is to
provide a process for constructing molecule-based
microelectronic devices on silicon substrates which can
easily be integrated with solid state silicon devices for
signal processing.

15 Still another object of the invention is to
provide small, sensitive, and specific microelectronic
devices with very low power requirements.

20 A further object of the invention is to provide
diodes, transistors, sensors, surface energy storage
elements, and light-emitting microelectrode devices which
can be controlled by molecular-level changes in
electroactive polymer components.

Summary of the Invention

25 The present invention is a process for making
microelectronic devices which can be controlled by

1 molecular-level changes in electroactive polymer
components. These devices are fabricated by
functionalizing electrodes formed by deposition of metal
on silicon dioxide substrates using convention masking and
5 photolithography techniques with polymers whose physical
properties change in response to chemical signals. The
key features are the small dimension of the electrodes and
the small spacing, in the range of less than five microns,
between them.

10 In one embodiment, an analogue of a solid state
transistor, wherein a transistor is defined as a material
whose resistance can be adjusted by an electrical signal,
is formed from an array of gold microelectrodes
derivatized with a redox polymer such as polypyrrole.
15 When polypyrrole is oxidized, it conducts an electrical
current between the microelectrodes. As in a solid state
transistor, the current between the two outer
microelectrodes of the array can be varied as a function
of the potential of the polymer electrically connecting
20 the electrodes in a manner analagous to the "gate" of a
transistor. As the potential is altered, the oxidation or
reduction of the polypyrrole can be effected. This device
amplifies the very small signal needed to turn the
polypyrrole from its reduced and insulating state to its
25 oxidized and conducting state. Further variations are

1 possible using additional polymers with different redox
potentials.

5 In a second embodiment, a diode is fabricated on
a silicon dioxide-silicon substrate from an array of two
or more microelectrodes separated from each other by a
distance of 2 microns or less, individually functionalized
with a chemically responsive polymer, such as a redox
polymer. Examples of redox polymers are polypyrrole,
poly-N-methylpyrrole, polythiophene, poly-3-methyl-
10 thiophene, polyvinylferrocene, derivatized styrene and
polyaniline. As many different polymers may be used as
there are pairs of microelectrodes. Since the polymers
respond at different potentials, each pair of electrodes
can be effectively isolated from the other
15 microelectrodes.

20 In yet another embodiment, a microelectronic-
device with transistor or "triode-like" properties is
fabricated by deposition of polyaniline onto an array of
two or more gold microelectrodes. Polyaniline, a redox
polymer, has the unusual property of being insulating at
an electrical potential, less than +0.1 V vs. SCE in
aqueous 0.5 M NaHSO₄, greater than 10⁶ times more
conducting at a slightly higher electrical potential, +
0.4 V vs. SCE in 0.5 M NaHSO₄, and insulating at a higher
25 electrical potential, +0.7 V vs. SCE in 0.5 M NaHSO₄. The

1 exact potential at which the polyaniline is conducting or
insulating is determined by the medium, the amount of
polyaniline connecting the electrodes, and interactions
with other polymers. This device is particularly useful
5 as an electrical switch between a specific range of
potentials or as a pH or other chemical sensor. The
device may be further modified for use as an oxygen or
hydrogen sensor by connecting the polyaniline to a noble
metal electrode such as a platinum electrode or by
10 dispersing particles of noble metals such as palladium
into the polyaniline.

Other specific embodiments of the present
invention include surface energy storage elements and
light-emitting microelectrodes.

15

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of a surface
energy storage device wherein electrical energy is used to
charge the device by reducing a polyviologen polymer,
20 $(PQ^{2+/-})_n$, and oxidizing a polyvinylferrocene polymer,
 $(FeCp_2^{+/-})_n$.

25

Fig. 2 is a cross-sectional view of a molecule-
based transistor consisting of three gold microelectrodes,
derivatized with polypyrrole and immersed in electrolyte,
with a schematic showing how the electrical potential of

1 the gate is set using a potentiostat with a counter
electrode and a saturated calomel reference electrode
(SCE).

5 Fig. 3 is a graph showing the output
characteristics of the transistor of Fig. 2 as I_D , the
current between source and drain, as a function of V_D , the
potential between source and drain, at various fixed gate
potentials, V_G .

10 Fig. 4a is a cross-sectional view of a molecule-
based transistor, consisting of two gold electrodes coated
with polyvinylferrocene, $(FeC_{P2}^{+/-})_n$, and polyviologen,
 $(PQ^{2+/+})_n$, and functionalized with a quinone-based
polymer, $(Q/QH_2)_n$, having a pH-dependent redox potential
which is more negative or positive than the potential of
15 the viologen polymer, depending on the pH.

Fig. 4b is a schematic of the effect of pH
variation on the polymers in the transistor of Fig. 4a and
shows the approximate relationship of the redox
potentials.

20 Fig. 5 is a cross-sectional view of a molecule-
based diode consisting of two gold microelectrodes
derivatized with two polymers of different redox
potentials.

25 Fig. 6 is a cross-sectional view of an array of
eight gold microelectrodes derivatized with different
amounts of polypyrrole.

1 Fig. 7 is a graph of cyclic voltammograms at 100
mV/s for an array like that in Fig. 6 in $\text{CH}_3\text{CN}/0.1\text{M} \text{[n-}$
5 $\text{Bu}_4\text{N}]\text{ClO}_4$. The bottom portion of the sketch is the
expected result based on the derivatization procedure and
electrochemical response.

10 Fig. 8a is a graph of the potential, V vs. SCE,
measure in $\text{CH}_3\text{CN}/0.1\text{M} \text{[n-}\text{Bu}_4\text{N}]\text{ClO}_4$, of five gold
microelectrodes connected with polypyrrole when one is
under active potential control at -1.0 V vs. SCE and one
15 is at a positive potential at which the polypyrrole is
expected to be conducting.

15 Fig. 8b is a graph of the potential, V vs. SCE,
of five gold microelectrodes connected with polypyrrole
where only one electrode is under active potential
control.

20 Fig. 9 is a graph of the current, i, measured
between electrodes, versus applied potential, V_{appl} vs.
SCE, for two adjacent microelectrodes connected with
polypyrrole as a function of V_{set} , where V_{set} is the fixed
25 potential vs. SCE of one of the two electrodes, and V_{appl} ,
where V_{appl} is the potential of the other electrode.

25 Fig. 10 is a graph comparing the diode
characteristics for two microelectrodes connected with (a)
polypyrrole and (b) poly-N-methylpyrrole where the fixed
potential, V_{set} , in (a) is -1.0 V vs. SCE and in (b) is
-0.6 V vs. SCE.

1 Fig. 11 is a cross-sectional view of a light-emitting pair of microelectrodes wherein the two gold
5 microelectrodes are connected by a polymer such that application of a voltage, approximately 2.6 V, results in emission of light characteristic of an excited tris, 2, 2'-bipyridine ruthenium (II) complex, $\text{Ru}(\text{bpy})_3^{2+}$.

10 Fig. 12 (inset) is a cross-sectional view of a device fabricated from two polyaniline-coated gold microelectrodes wherein V_D is the potential between one microelectrode "source" and another microelectrode "drain" at a fixed gate potential, V_G , controlled relative to an aqueous saturated calomel reference electrode (SCE).

15 Fig. 12a is a graph of the drain current, I_D , in microamps versus the drain voltage, V_D , in mV for the device shown in the inset at various values of V_G , where the charge passed in setting the gate to a potential where there is conductivity between source and drain can be regarded as an input signal.

20 Fig. 12b is a graph of I_D vs. V_G at a fixed V_D of 0.18 V for the device shown in the inset.

25 Fig. 13 is a graph of a cyclic voltammogram at 100 mV/s for a device such as the one described in Fig. 12 (inset) when V_G is +0.3 V vs. SCE and V_D is 20 mV. ---- is at 0 hours and is after 16 hours.

1 Fig. 13 (inset) is a graph of I_D versus time in
hours when V_D is at 20 mV, V_G is at +0.3 V vs. SCE, and
the electrolyte is 0.5 M NaHSO₄ at pH 1.

5 Fig 14a is a graph of the I_D vs. V_G for a device
such as the one shown in Fig. 12 (inset), where V_G is
varied from -0.2 V vs. SCE to +0.8 V vs SCE.

Fig. 14b is a graph of resistance in ohms versus
 V_G for a device such as the one in Fig. 12 (inset).

10 Fig. 15 is a graph for a device such as the one
shown in Fig. 12 (inset) of I_D in microamps versus V_D in
mV at a V_G of -0.2 V vs. SCE, a potential at which
polyaniline is reduced and insulating.

15 Fig. 16 is a graph of I_D versus time in seconds
at V_D of 0.18 V for a device such as the one shown in Fig.
12 (inset) for a V_G step of -0.2 to +0.3 V vs SCE.

Fig. 17 is a cross-sectional view of a
polyaniline-connected microelectrode array connected
externally to a macroscopic indicator electrode.

20 Fig. 18 is a cross-sectional view of a
polyaniline-connected microelectrode array consisting of
three gold microelectrodes connected to a counter-
electrode, reference electrode, and potentiostat.

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Detailed Description of the Invention

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The present invention is a process for producing molecule-based microelectronic devices consisting of two or more microelectrodes separated by a small dimension, which can be contacted individually and independently functionalized using electroactive polymers with specific properties that are responsive to chemical and/or electrical signals. Examples of one group of electroactive polymers are redox polymers which are insulating when reduced and conducting when oxidized.

15

20

The microelectrodes are small, typically on the order of 2 to 5 microns wide by 50 to 150 microns long by 0.1 to 0.15 microns thick, although even smaller electrodes may be utilized, and made of inert, electrically conductive material such as gold, silver, palladium, gold-platinum, and gold-palladium or other metals that are electrochemically inert. The conductor should be easily deposited and have low electrical resistance, good adhesion to the substrate, stability, and ability to be functionalized.

25

These electrodes are positioned on an inert substrate. An example of a preferred substrate would be oxidized silicon wafers made by growing a 4500 Angstroms to 10,000 Angstroms thick SiO_2 layer on $\angle 100 \rangle$ Si. Devices made according to the present invention on silicon wafers

1 may be easily integrated into presently available solid
state microelectronic devices, most of which are also
produced on silicon wafers.

5 The small separation between electrodes,
typically on the order of 0.1 to 2 microns, combined with
the use of electroactive polymers with specific
properties, is crucial to the invention. The smallest
inter-electrode space technically feasible is preferred.
The small inter-electrode space allows high current
10 densities. As the distance between microelectrodes is
increased, output decreases and "noise" increases. The
direction of current flow, the ability to respond to a
chemical signal such as a change in pH, the rate of
response, the degree of response, the storage of energy,
15 and the ability to place other pairs of electrodes in
close proximity without interference is due to the choice,
deposition, degree of separation and quantity of polymer.

20 Various groups of polymers known to those
skilled in the art are suitable for use in the present
invention. The requirements for such polymers are that
they can be electrochemically deposited on individual
electrodes and polymerized and that they can respond to a
signal, in a reversible manner, in a way which can be
25 electrochemically detected. Such materials are described
by R.W. Murray in Electroanalytical Chemistry, Vol. 13,
Edited by A.J. Bard (Marcel Dekker, N.Y., 1984).

1 Suitable electrochemically polymerizable
materials for use in the present invention include redox
polymers. Examples of such polymers are polypyrrole,
5 polyaniline, poly-N-methylpyrrole, polythiophene, poly-3-
methylthiophene and polyvinylferrocene (poly vinyl
dicyclopentadienyliron). Styrene and vinyl aromatic
derivatives such as vinyl pyridine, vinyl,2,2'-bipyridine
and metal complexes of these derivatives, are also useful
since they can be electrochemically polymerized and may be
10 derivatized with a number of reagents, including
biologically active agents such as enzymes and ionophores
that complex with ions such as lithium and calcium.

15 Using two or more electrodes connected with one
polymer, a transistor-like device may be fabricated. By
choosing two or more polymers with different redox
potentials, adjacent electrodes may be electronically
isolated or made to function as diodes or surface energy
storage units.

20 For polypyrrole and poly-N-methylpyrrole, the
oxidized materials are electronic conductors. The
conductivity varies by more than 10^{10} depending on the
redox state of the polymers. The consequence of the very
large difference in conductivity with redox state is that
25 the potential drop can occur across a very small fraction
of length of the connecting polymer when one

1 microelectrode is held at a potential where the polymer is
reduced and insulating and the other is held at a
potential where the polymer is oxidized and conducting.
For example, polypyrrole is insulating at approximately
5 -0.4 V vs. SCE potential but becomes conducting at
positive potentials up to any positive potential at which
the polypyrrole is durable. The actual conductivities of
the oxidized polymers, measured in $\text{CH}_3\text{CH}/0.1 \text{ M} [\text{n-}$
10 $\text{Bu}_4\text{N}] \text{ClO}_4$, of polypyrrole and poly-N-methylpyrrole,
respectively, are approximately $10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ and 10^{-4}
15 to $10^{-5} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

In contrast to polypyrrole, polyaniline can be
made conducting by either a positive or a negative shift
of the electrochemical potential, since polyaniline is
essentially insulating at sufficiently negative (negative
20 of 0.0 V vs. SCE) or positive (positive of +0.7 V vs. SCE)
electrochemical potentials. As a result, a polyaniline-
based device responds to a signal in a significantly
different way from solid state transistors where the
current passing between source and drain, I_D , at a given
source to drain voltage, V_D , does not decrease with
increasing gate voltage, V_G . The conductivity of
25 polyaniline has been measured to span eight orders of
magnitude and is sensitive to pH and other chemical
parameters.

1 The potential at which a polymer exhibits a
sharp change in conductivity due to oxidation is the
threshold potential, V_T . V_T can be manipulated by using
different monomers or different redox polymers, and by
5 varying the medium to be "seen" by the polymer.

10 Other polymers which are useful in the present
invention include redox polymers known to be
electrochromic materials, compounds which change color as
a result of electrochemical reactions. Examples of such
10 materials are polyvinylferrocene, polynitrostyrene and
viologens. Viologens, described by Wrighton et al. in
U.S. Patent Nos. 4,473,695 and 4,439,302, are compounds
formed from 4,4'-bipyridinium which may be polymerized and
covalently bonded or otherwise confined to the surfaces of
15 electrodes. Viologens such as dialkyl-4,4'-bipyridinium
di-cation and associated anions, dichloride, dibromide, or
di-iodide, form contrasting colors when oxidized or
reduced. Since each monomer unit of viologen has a 2+
charge which is balanced in the presence of two halide
20 counter ions, the counter ions can be replaced with a
complex ion such as PtCl_6^{2-} which can then be reduced to
yield embedded elemental Pt(0) in highly dispersed form.
An enzyme such as hydrogenase can also be immobilized onto
or throughout the redox polymer to equilibrate the redox
25 polymer with the enzyme substrates.

1 Substituted viologens are useful for photogeneration of hydrogen from aqueous electrolytes, for reduction of metal-containing macromolecules, and on p-type silicon photocathodes in electrolytic cells.

5 The invention is further illustrated by the following non-limiting examples. Devices in these examples were constructed according to the procedure outlined below, with minor variations.

10 Fabrication of Microelectrode Arrays

Microelectrode arrays were fabricated in the Massachusetts Institute of Technology Microelectronics Laboratory in the Center for Materials Science and Engineering which includes a class 100 clean room and is equipped to meet the specialized requirements for the production of solid state microelectronic devices such as "silicon chips".

20 A two-mask process was designed. The first mask was made for a metal lift-off procedure to form microelectrodes, leads, and contact pads. The second mask was made to pattern a photoresist overlayer leaving a 50 to 140 micron length of the microelectrodes and the contact pads exposed.

25 A microelectrode array was designed using the Computer Aided Design Program HPEDIT at a Hewlett Packard

1 Model 2648A graphics terminal on a DEC-20. The design
file was translated into Caltech Intermediate Form
(CIF). This CIF file was translated to Mann compatible
code and written on magnetic tape. Masks for
5 photolithography were made from the file on magnetic tape
using a Gyrex Model 1005A Pattern Generator. E-K 5" X 5"
X 0.090" Extra Flat high resolution glass emulsion plates
were used to make the photolithography masks. The
emulsion plates were developed by a dark field process.

10 p-Si wafers of 100 orientation, two inches in
diameter and 0.011 inches thick, obtained from Wacker
Corp. were used as substrates upon which to fabricate the
microelectrode arrays. The silicon wafers were RCA
cleaned in a laminar air flow hood in the class 100 clean
15 room. The wafers were immersed in hot aqueous 6% by
volume H_2O_2 /14% by volume aqueous NH_3 , briefly etched in
hydrofluoric acid diluted 10:1 with deionized water,
immersed in hot aqueous 6% by volume H_2O_2 /14% by volume
 HCl , rinsed in deionized water (resistance greater than 14
20 Mohm cm), and spun dry. The cleaned wafers were loaded
immediately into an oxidation tube furnace at 1100°C under
 N_2 . For examples 1 to 5, a dry/wet/dry/anneal oxidation
cycle was used to grow a thermal oxide layer 4500
Angstroms thick. For example 6, a dry oxidation cycle was
25 used to grow a thermal oxide 11850 Angstroms thick. Oxide

1 thicknesses were measured using a Gaertner Model L117
5 ellipsometer. The oxidized wafers were taken immediately
10 to the photolithography stage.

 Each oxidized wafer was flood-coated with
5 hexamethyl-disilazane and spun at 6000 rpm for 20 sec.
10 For examples 1 to 5, one ml of MacDermid Ultramac PR-914
15 positive photoresist was syringed onto each wafer. The
20 wafer coated with resist was spun for 30 sec at 4000 rpm
25 and then prebaked 35 min at 90°C. For example 6, one ml of
30 Shipley 1470 positive photoresist was syringed onto each
35 wafer and the wafer spun for 30 seconds at 6000 rpm. The
40 coated wafer was then prebaked 25 minutes at 90°C.

 A GCA Mann 4800 DSW Wafer Stepper was used to
15 expose the photoresist. The Mann uses the 405 nm line of a
20 350 W Hg arc lamp as a light source. The mask image is
25 reduced 5:1 in the projection printing. For examples 1 to
30 5, an exposure time of 0.850 sec was used and the
35 photoresist developed 60 sec in MacDermid Ultramac MF-62
40 diluted 1:1 with deionized water. For example 6, the wafer
45 was exposed for 1.2 seconds and developed 60 seconds in
50 Shipley 312 developer diluted 1:1 with dionized water.
55 The developed wafers were then cleaned in a planar oxygen
60 etching chamber at 75-100 W forward power in 20 mtorr of
65 oxygen for 15 seconds.

1 A bilayer metallization was performed. A MRC
8620 Sputtering System was used in preparing the
microelectrode arrays of examples 1 to 5. The bilayer
metallization of the wafers used in example 6 was
5 performed in a NRC 3117 electron beam evaporation
system. Wafers were placed on a quartz plate that was
freshly coated with chromium. The wafers were
backspattered 2 min at 50 W forward power in an argon
plasma at 5 mtorr. Chromium was sputtered at 50 W forward
10 power to produce a layer of chromium. The layer on the
wafers in examples 1 to 5 was 200 Angstroms thick. The
layer in example 6 was 50 Angstroms thick. Gold was then
sputtered at 50 W forward power to produce a layer 1000
15 Angstroms thick. Chromium serves as an adhesion layer for
the gold. The combined chromium/gold thickness of the
wafers used in example 6 was measured to be 1052 Angstroms
on a Dektak II surface profile measuring device.

20 At this point, the chromium/gold was in direct
contact with the SiO_2 substrate only in the areas that
were to form the microelectrodes, leads, and contact pads
and on photoresist in all other areas. The chromium/gold
on photoresist was removed by a lift-off procedure: the
metallized wafers were immersed in warm acetone, in which
soft-baked positive photoresist is soluble, for 75 minutes
25 for the wafers used in examples 1 to 5 and 5 minutes for

1 the wafers used in example 6. The wafers used in examples
1 to 5 were briefly sonicated in acetone to remove the
metal between microelectrodes, dried, and then cleaned of
residual photoresist in a planar oxygen plasma etching
5 chamber at 200 W forward power in 50 mtorr oxygen for 60
sec.

10 The wafers used in example 6 was blasted with
acetone from a Paasche air brush with N₂ at 70 psi,
sonicated for 30 minutes in acetone, then rinsed with
acetone and methanol before drying. The wafers were then
cleaned in a mixture of hot aqueous 6% by volume H₂O₂/14%
by volume aqueous NH₃, rinsed in deionized water (greater
than 14 megaohm·cm), and spun dry. The wafers were then
baked at 180°C for 40 minutes before repeating the
15 photoresist spin coating process. The wafers were again
prebaked at 90°C for 25 minutes and then exposed in a Karl
Suss Amercia Inc. Model 505 aligner for 11 seconds, using
a dark field mask. The photoresist was developed in
Shipley 312 developer diluted 1:1 with deionized water to
20 expose the bond pads and the array of microelectrode
wires. The exposed areas were cleaned of residual
photoresist in the oxygen plasma etching chamber at 75-100
W for 1 minute. The remaining photoresist was hardbaked
at 180°C for 15 hours.

1 Wafers were then baked at 180°C for 40 minutes
before repeating the photoresist spin coating process.
The wafers were again prebaked at 90°C for 25 minutes and
then exposed in a Karl Suss American Inc. Model 505
5 aligner for 11 seconds, using a dark field mask. The
photoresist was developed to Shipley 312 developer diluted
1:1 with deionized water to expose the bond pads and the
array of microelectrode wires. The exposed areas were
cleaned of residual photoresist in the oxygen plasma
10 etching chamber at 75-100 W for 1 minute. The remaining
photoresist was hard baked at 180°C for 15 hours.

15 Individual die (chips) were scribed and
separated. The chips were mounted on TO-5 headers from
Texas Instruments with Epoxi-Patch 0151 Clear from Hysol
Corp. A Mech-El Ind. Model NU-827 Au ball ultrasonic
wire bonder was used to make wire bonds from the chip to
the TO-5 header. The leads, bonding pads, wire bonds, and
header were encapsulated with Epoxi-Patch*0151. The
header was connected through a TO-5 socket to external
20 wires. The external wires were encased in a glass tube.
The header was sealed at the distal end of the glass tube
with heat shrink tubing and Epoxi-Patch 1C white epoxy
from Hysol Corp.

25 Prior to use as a microelectrode array, the
array was tested to establish the leakage current between

* Trade mark

1 the various electrodes of the array. Arrays characterized
as usable have a measured resistance between any two
electrodes of greater than 10^9 ohms in non-aqueous
electrolyte solution containing no added electroactive
5 species. In many cases only a fraction of the electrodes
of an array were usable. Prior to use in experimentation
the microelectrode arrays were tested further in aqueous
electrolyte solution containing 0.01M $K_3[Fe(CN)_6]$ and 0.01
M $K_4[Fe(CN)_6]$ or with $[Ru(NH_3)_6]Cl_3$ to establish that the
10 microelectrodes give the expected response. Typically, a
negative potential excursion to evolve H_2 cleaned the gold
surface sufficiently to give good electrochemical response
to the $Fe(CN)_6^{3-/4-}$ or $Ru(NH_3)_6^{3+/2+}$ redox couples. The
electrolyte used for electrical measurement was 0.1 M
15 $NaClO_4$ in H_2O solvent, 0.5 M $NaHSO_4$, or 0.1 M $[n-Bu_4N]ClO_4$
in CH_3CN solvent.

Electrochemical Equipment

20 Most of the electrochemical experimentation in
examples 1 to 5 was carried out using a Pine Model RDE 3
bipotentiostat and potential programmer. In cases where
two microelectrodes were under active potential control
and a third was to be probed, a PAR Model 363
potentiostat/galvanostat was used in conjunction with the
25 Pine Model RDE 3. All potentials were controlled relative

1 to an aqueous saturated calomel reference electrode
(SCE). Typically, electrochemical measurements were
carried out under N_2 or Ar at 25°C.

5 For example 6, most of the electrochemical
experimentation was carried out using a Pine Model RDE 4
10 bipotentiostat and potential programmer. In some cases
where only a single potentiostate was needed a PAR Model
173 potentiostat/galvanostat and a PAR Model 175 universal
programmer was used. Potential step experiments were
carried out using the RDE 4 with a Tektronix type 564B
15 storage oscilloscope as the recorder.

Derivatization of Microelectrodes

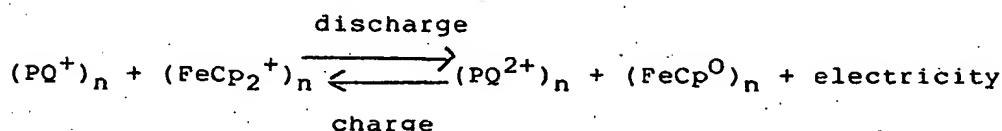
20 In examples 1 to 5, the gold microelectrodes
were functionalized by oxidation of 25-50 mM pyrrole or N-
methylpyrrole in $CH_3CN/0.1 \text{ M } [n\text{-}Bu_4N]ClO_4$. The
polypyrrole was deposited at +0.8 V vs. SCE, and the poly-
N-methylpyrrole was deposited at +1.2 vs. SCE. The
deposition of the polymer can be effected in a controlled
manner by removing the array from the derivatization
25 solution after passing a certain amount of charge.
Electrodes were then examined by cyclic voltammetry in
 $CH_3CN/0.1 \text{ M } [n\text{-}Bu_4N]ClO_4$ to assess the coverage of polymer
and to determine whether the polymer coated two or more
electrodes resulting in a "connection" between them.

1 Prior to use as a microelectrode array, each
microelectrode wire in the devices used in example 6 was
tested with an ohmmeter to make sure it was not shorted to
any other wire on the device. Then each microelectrode
5 was tested by running a cyclic voltammogram in 0.01 M
 $\text{Ru}(\text{NH}_3)_6^{3+}/0.1\text{M}$ $\text{NaNO}_3/\text{H}_2\text{O}$. The microelectrodes were
derivatized by oxidation of a stirred 0.44 M aniline
solution in 0.5 M $\text{NaHSO}_4/\text{H}_2\text{O}$ at pH 1. The polyaniline was
deposited at +0.9 V vs. SCE. Electrodes were then
10 examined by cyclic voltammetry in 0.5 M NaHSO_4 at pH 1 to
assess the coverage of polymer and to determine whether
the polymer coated two or more electrodes resulting in a
connection between them. Macroscopic gold electrodes were
15 derivatized with polyaniline by the same procedure to
accurately relate the thickness of polyaniline to cyclic
voltammetry response and the charge passed in the anodic
deposition. Typically, a portion of the gold flag was
covered with grease prior to depositing the polyaniline
over the exposed gold surface. The grease was then
20 removed with CH_2Cl_2 to give a well defined step from gold
to polyaniline.

Example 1

25 In one embodiment of the present invention,
depicted in Fig. 1, a surface energy storage device 10 is

1 constructed from two gold microelectrodes 12, 3 microns
 wide by 140 microns long by 0.12 microns thick, deposited
 on a 1 micron thick SiO_2 insulator 14 grown on a 100 Si
 substrate 16 and separated by a distance of 1.4 microns.
5 Each microelectrode is individually coated with
 electrochemically deposited and polymerized polymers,
 polyviologen 18 and polyvinylferrocene 20. Electrical
 energy can be used to charge the device by reducing the
10 polyviologen, the $(\text{PQ}^2+)_n$ polymer, and oxidizing the
 polyvinylferrocene, the $(\text{FeCp}_2^0)_n$ polymer, according to
 the following reaction:



Example 2

20 In another embodiment of the present invention,
 shown in Fig. 2, a molecule-based transistor 22 is
 fabricated from three gold microelectrodes separated by
 1.4 microns, derivatized with polypyrrole 24. Typical
 coverage of the polypyrrole is 10^{-7} mol/cm² of exposed
 gold, and the individual microelectrodes are electrically
 connected. The microelectrodes are wired so as to
25 correspond to the drain 26, gate 28, and source 30 as in a
 conventional solid state transistor.

1 The properties of the device are characterized
by immersing the device in an electrolyte, $\text{CH}_3\text{CN}/0.1\text{M} [\text{n}-$
5 $\text{Bu}_4\text{N}]\text{ClO}_4$, and measuring the current 32 between source 30
and drain 26, I_D , as a function of the potential 34
between source and drain, V_D , at various fixed gate
potential 36, V_G . The results are shown in Fig. 3.

10 At values for V_D of less than 0.5 V, the device
is "off" when V_G is held at a negative potential where the
polypyrrole is expected to be insulating and I_D is
small. When V_G is moved to potentials more positive than
15 the oxidation potential of polypyrrole, approximately -0.2
V vs. SCE, the device "turns on" and a significant steady-
state value for I_D can be observed for modest values of
 V_D . The close spacing of the microelectrodes allows an
easily measurable current to pass between the source 30
and the drain 26 when V_D is significant and V_G is above
the threshold, V_T . V_T , the gate potential at which the
device starts to turn on, is approximately equal to the
20 redox potential of polypyrrole. For V_G more positive than
 V_T , the value of I_D increases at a given value of V_D , in a
manner consistent with the increasing conductivity due to
an increasing degree of oxidation. At sufficiently
positive values of V_G , greater than or equal to +0.5 V vs.
25 SCE, I_D becomes insensitive to further positive movement
of V_G at a given value of V_D , a result consistent with

1 measurements of the resistance of the oxidized polypyrrole
coated on a microelectrode array. A small range of V_D
values (0 to 0.2 V) is used to minimize electrochemical
reactions at the source 30/polymer 24 and drain 26/polymer
5 24 interfaces.

A fraction of $10^{-8}C$ of charge is required to
obtain the maximum steady-state value of I_D when V_D is
equal to 0.2 V with this device. The value of I_D
achievable with the device is $4 \times 10^{-5}C/s$. It is apparent
10 from these results that a small signal to the gate
microelectrode can be amplified in much the same way that
a small electrical signal can be amplified with a solid
state transistor. The major difference is that the turn
on/turn off time in the molecule-based system is dependent
15 on the rate of a chemical reaction rather than on electron
transist times across the souce to drain distance. For
the molecule-based system, the properties such as V_T and
minimum turn on signal can be adjusted with rational
variation in the monomer used to prepare the polymer. Use
20 of smaller dimensions and materials other than polypyrrole
can also lead to faster switching times.

Example 3

As shown in Fig. 4a, a molecule-based pH sensor
25 40 can theoretically be fabricated using a two
microelectrode array on a SiO_2 -Si substrate 42.

1 The two gold microelectrodes 44, 45 are coated
with polyviologen 46, $(PQ^{2+}/^+)_n$, and polyvinylferrocene
48, $(FeCp_2^{+/0})_n$, respectively, and then overlaid with
another polymer 50 with a different pH dependent redox
5 potential, such as a polyquinone, $(Q/QH_2)_n$, whose redox
potential is above the redox potential of the polyviologen
at high pH and between that of the polyviologen and
polyvinylferrocene at low pH.

10 The pH variation serves as the signal to be
amplified. Varying the pH results in a variation in
current passing between the two gold electrodes at a fixed
potential difference with the negative lead to the
viologen coated electrode. As shown by Fig. 4b,
alteration of the pH changes the redox potential of
15 polymer 50. Low pH acts to make it easier to reduce
polymer 50. Current can flow between source 44 and drain
45 when the negative lead is attached to the polyviologen-
coated gold microelectrode 44 and the positive lead is
connected to the polyvinylferrocene-coated gold
20 microelectrode 45 and the redox potential of the
polyquinone is between the redox potentials of the two
polymers 46 and 50 coating source 44 and drain 45. At a
fixed potential difference, the current passing between
the two microelectrodes 44 and 45 should depend on the pH
25 of the solution contacting the polymer 50.

1 A pH sensor may also be fabricated by coating a
microelectrode array with a polymer such as polyaniline.
For a device consisting of two gold microelectrodes, 0.1
micron thick, 4.4 microns wide, and 50 microns long,
5 separated by a distance of 1.7 microns, coated with a
layer of polyaniline approximately 5 microns thick,
changes in the pH of the surrounding medium markedly alter
the conductivity. For example, the value of I_D at V_D
10 equal to 20 mV and V_G of 0.2 V vs. SCE is reduced upon
raising the pH of the solution, where I_D is the current
between one electrode and the next, V_D is the potential
between the first and second electrode, and V_G is the
potential between the two electrodes and a saturated
calomel reference electrode. I_D at pH 1 is approximately
15 10^2 times greater than at pH 6.

Polyaniline is limited to use with solutions of
pH less than 6 to preclude irreversible chemical changes
that occur at the higher pH values. However, other pH-
sensitive redox polymers may be used to fabricate
20 microelectrode pH-sensors for other pH ranges.

Numerous uses in chemical systems are possible
for such sensing devices. For example, such a device may
be used to detect subtle changes in pH of aqueous
solutions. Electrical signals generated by the device
25 could be directly amplified and processed further.

1

Example 4

A molecule-based diode 50, produced according to the present invention, is shown in Fig. 5.

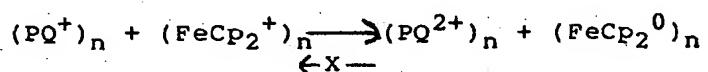
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Microelectrodes 52 and 54 are each individually covered with polymers 56 and 58 having very different redox potentials. The current passes between the two heavily coated, connected microelectrodes 52 and 54 as a function of the threshold potential of the diode, which is dependent on the redox potentials of the polymers.

10

Electrons only flow from microelectrode 52 to microelectrode 54 due to the large difference in the redox potentials of the two polymers 56 and 58. For example, for a polyviologen/-polyvinylferrocene diode, charge will pass only when the negative lead of the applied potential is connected to the gold electrode 52 coated with polyviologen 56 and the positive lead is attached to the gold electrode 54 coated with polyvinylferrocene 58. This reaction is shown as:

20



As shown in Fig. 6, it is possible to electro-chemically deposit electroactive polymers 60 on individual electrodes 62a-h in variable amounts. The electrodes 62e-

25

1 h which are bridged by the polymer 60 are electrically
2 connected: charge can pass from one microelectrode 62e to
3 another microelectrode 62f-h via conduction mechanisms of
4 the polymer 60. Connected electrodes are typically
5 associated with coverages of approximately 10^{-7} mol
6 polymer/cm² electrode. Addressing one electrode oxidizes
7 and reduces the polymer 60 over all of the electrodes
8 62e-h.

9 Fig. 7 shows the cyclic voltammetry of the
10 polypyrrole modified array of Fig. 6 in $\text{CH}_3\text{CN}/0.1\text{M} [\text{n}-$
11 Bu_4ClO_4 containing no added redox active species. The
12 unfunctionalized electrodes 62a, 62b, and the electrode
13 62c, with a negligible amount of polypyrrole, lack the
14 cyclic voltammetry signal characteristic of an electrode-
15 confined polymer. Immediately adjacent to the non-
16 derivatized electrodes 62a-c are electrodes 62d-h that
17 show cyclic voltammograms characteristic of electrode-
18 confined polypyrrole. The shape of the voltammogram is
19 nearly the same as for a macroscopic gold electrode
20 derivatized in the same manner. In addition, the
21 potential of the oxidation and reduction peaks are as
22 expected for the oxidation and reduction of polypyrrole.

23 Based on the integration of the charge passed
24 upon cycling the derivatized microelectrodes 62
25 individually between the negative and positive limits, it

1 can be seen that controlled amounts of polypyrrole 60 can
be deposited on the electrodes 62. The same results, with
the expected differences in the oxidation and reduction
potentials, were shown using poly-N-methylpyrrole instead
5 of polypyrrole.

10 Figs. 8a and 8b show the spatial potential
distributions across a polypyrrole array 70 where one
(Fig. 8b) or two (Fig. 8a) of the electrodes is under
active potential control. The entire array 70 was
immersed in $\text{CH}_3\text{CN}/0.1\text{M} [\text{n-Bu}_4]\text{ClO}_4$ and a biopotentiostat
15 used to actively control the potential of one (Fig. 8b) or
two (Fig. 8a) microelectrodes against a common reference
and counter electrode in the electrolyte solution.

20 The potential of one microelectrode 72 in the
five electrode array 70 was set at a negative potential of
-1.0 V vs. SCE and the potential of another microelectrode
25 74 varied between 0.0 and 1.0 V vs. SCE.

25 As shown in Fig. 8a, the potentials of
electrodes 76, 78, and 80 not under active potential
control are nearly equal to the positive potential applied
to electrode 74. Although a small potential drop of
approximately 50 mV occurs over the 9 micron distance
separating electrodes 74 and 80, the essential finding is
that nearly all, up to 1.8 V, of the potential drop occurs
across a narrow region immediately adjacent to electrode

1 72 under active potential control at -1.0 V vs. SCE. The
result is consistent with the difference in conductivity
between the reduced and oxidized state of the polypyrrole,
of which the consequence is that the potential drop occurs
5 across a very small fraction of length of the connecting
polymer when one microelectrode is held at a potential
where the polymer is reduced and insulating and another is
held at a potential where the polymer is oxidized and
conducting. This would not be an expected result for a
10 polymer with only a moderate conductivity, such as those
that exhibit redox conductivity where a linear change in
concentration of redox centers across the thickness
spanned by two electrodes at differing potentials would
give a potential profile predicted by the Nernst equation.

15 Fig. 8b shows that when only one 82 of the
microelectrodes is under active potential control in the
positive region, all of the electrodes are at the same
potential as would be expected when there is an electrical
connection between them. When one of the microelectrodes
20 is driven to a negative potential, it would be expected
that all would ultimately follow. Upon reduction,
however, the polymer becomes insulating and the rate of
potential following can be expected to be slower.

25 As shown by the current vs. potential data in
Fig. 9, polypyrrole connected-microelectrodes 90 behave in

1 a diode-like fashion. Current vs. V_{applied} curves are
shown as a function of the potential, V_{set} , at which one
92 of the electrodes is fixed relative to the SCE. The
current measured is that passing between the two
5 microelectrodes. The magnitude of the current passing
through the other microelectrode is identical to that
passing through the other microelectrode but opposite in
sign.

When V_{set} is sufficiently positive, the current
10 vs. V_{applied} curve is linear over a wide range of
 V_{applied} . The resistance of polypyrrole from the slope of
such plots is about 10^3 ohms. Current densities exceeding
1 KA/cm^2 were observed. When V_{set} is sufficiently
negative, there is a broad range of the current vs.
15 V_{applied} curve where there is insignificant current.
Therefore, as shown in Fig. 10a, a good diode
characteristic can be obtained using polypyrrole coated,
closely spaced microelectrodes. The onset of current
closely corresponds to the situation where the V_{appl} .
20 results in the conversion of the polypyrrole from its
reduced and insulating state to its oxidized and strongly
conducting state.

As shown in Fig. 10b, results using poly-N-
methylpyrrole in place of polypyrrole in the array
25 shown in Fig. 9 were similar except that the value of V_{set}

1 necessary to obtain a current that is linear as V_{applied}
is varied is more positive than with polypyrrole. The
resistance of the poly-N-methylpyrrole is 10^5 to 10^6
ohms. Both the higher resistance and the more positive
5 potential necessary to obtain the conducting regime are
consistent with the known differences between polypyrrole
and poly-N-methylpyrrole.

Example 5

10 A light emitting device 98 may also be made
according to the process of the present invention. As
shown in Fig. 11, light is emitted from a polymer 100
overlaying two gold microelectrodes 102 on a silicon
dioxide-silicon substrate 104 when an electrical current
15 is applied. In the depicted device, light characteristic
of an excited $\text{Ru}(\text{bpy})_3^{2+}$ species is emitted when a voltage
of approximately 2.6 V is applied.

20 Polymers useful in a light emitting device
according to the present invention can be polymerized from
any monomers which are electrochemiluminescent, such as
vinyl derivatives of rubrene or diphenyl anthracene.

Example 6

25 A triode-like device was also constructed by
electrochemical deposition and oxidation of a polyaniline

1 film onto a microelectrode array consisting of eight gold
electrodes, 0.1 micron thick, 4.4 microns wide, and 50
microns long, each individually addressable and separated
from each other by 1.7 microns.

5 The magnitude of the current passing between
electrically connected microelectrodes at a given applied
potential depends on the electrochemical potential of the
polyaniline. In an electrolyte of aqueous 0.5 M NaHSO₄,
the current at a fixed applied potential is maximum at an
10 electrochemical potential of +0.4 V vs. SCE and declines
by a factor of greater than 10⁶ upon reduction to a
potential of + 0.1 V vs. SCE or oxidation to + 0.7 V vs.
SCE.

15 The polyaniline-functionalized microelectrodes
were examined by cyclic voltammetry in 0.5 M NaHSO₄ at pH
1 to assess coverage of the polymer and to determine
whether the polymer coating two or more electrodes results
in an electrical connection between them. Derivatization
of the electrode can be controlled by adjusting the amount
20 of polyaniline by varying the amount of charge passed in
the electrochemical polymerization. At one extreme, the
amount of polyaniline can be small enough to derivatize the
individual microelectrodes but not to electrically connect
them. At the other extreme, polyaniline can be deposited
25 in amounts sufficient to electrically connect all of the
microelectrodes.

1 Both a separate, unconnected microelectrode and
multiple, connected electrodes show the same cyclic
voltammogram at 50 mV/s in 0.5 M NaHSO₄ as does a single
5 unconnected reference microelectrode at 50 mV/s in 0.5 M
NaHSO₄. This is consistent with one electrode being
capable of oxidizing all of the polyaniline present on a
single microelectrode or on multiple connected micro-
electrodes. When adjacent derivatized microelectrodes are
not connected, the sum of the areas under the cyclic
10 voltammograms for the individual electrodes is the area
found when the microelectrodes are externally connected
together and driven as a single electrode. The thickness
of polyaniline is not measured to be directly proportional
to the integrated cyclic voltammetry wave as it is for
15 surface-confined, viologen derived polymers. This lack of
direct proportionality may be attributable to
morphological changes in the polymer with increasing
thickness.

20 As shown in Fig. 12 (inset), a triode-like
device 110 was constructed by coating two adjacent gold
microelectrodes 112, 114 with a five to 10 micron thick
electrochemically deposited and polymerized film of
polyaniline 116. Measurements were made by immersing the
25 device 110 in aqueous 0.5 M NaHSO₄ at 25°C under an inert
atmosphere of N₂ or Ar. Devices constructed in this
manner exhibit fairly long term stability.

1

As shown by the cyclic voltammogram in Fig. 13 for the device 110, the connected pair of electrodes exhibits a nearly constant steady state current between the two microelectrodes for at least 16 hours when V_D is 20 mV and V_G is 0.3 V vs. SCE. In general, devices can be used for characterization for several days without significant deterioration.

5

10

15

The conductivity of polyaniline which is immersed in an electrolyte such as aqueous 0.5 M NaHSO_4 depends on the electrochemical potential, which can be varied by varying V_G . As shown in Figs. 14a and 14b, the resistance of polyaniline depends on its electrochemical potential. The minimum resistance is at an electrochemical potential in the vicinity of +0.4 V vs. SCE. Changes in resistance in excess of 10^6 are routinely measured.

20

25

The minimum resistance for polyaniline is similar to that for polypyrrole connecting two microelectrodes spaced 1.4 microns apart, as shown in example 3. It is significantly different from polypyrrole, however, in that polyaniline is less conducting at potentials less than or greater than +0.4 V vs. SCE. The change in resistance of polyaniline is essentially reversible for potentials less than +0.6 V vs. SCE. Potentials significantly more positive than +0.6 V

1 vs. SCE yield an increase in the resistance of the
polyaniline when the potential is again decreased to +0.4
V vs. SCE. The limit of positive applied potential is
determined by O_2 evolution and limited durability of the
5 polyaniline. The limit of negative applied potential is
determined by the onset of H_2 evolution.

10 As shown in Figs. 12a and 12b, the triode-like
device 110 shows an increase and then a decrease in I_D as
 V_G is varied from negative to positive potentials, unlike
conventional solid state devices which show an increase in
15 I_D as V_G is varied until the I_D ultimately levels off at a
constant, V_G -independent value. The charge passed in
setting the gate to a potential where there is
conductivity between the source 114 and drain 112 can be
regarded as an input signal. For the device 110, the
charge necessary to completely turn on the device is
approximately $10^{-6} C$.

20 Transconductance, g_m , is determined by the
equation:

$$\frac{\partial I_D}{\partial V_G} \bigg|_{V_D} = g_m$$

Using the data in Figs. 12a and 12b, the maximum
value of g_m for device 110 is approximately 20
millisiemens per millimeter of gate width, as determined
25 from the rising part of the $I_D - V_G$ curve as V_G is moved
to a potential more positive than approximately 0.1 m /V.

1 By convention, gate length in Si/SiO₂/metal
field effect transistors (MOSFET) is the separation of
source and drain. "Width" therefore corresponds to the
long dimension of the device 110. Since the g_m of device
5 110 is only about one-order of magnitude less than that
for good MOSFET devices, the signal from the polyaniline-
based device can be fed to conventional MOSFET in the form
of voltage across a load resistance for further
amplification.

10 Diode-like behaviour can be obtained using
device 110, as shown in Fig. 15, at V_G values where the
polyaniline is reduced and insulating. Current passes
between the microelectrodes 112 and 114 when the "source"
microelectrode 114 is oxidized. If the "drain" micro-
electrode 112 is moved to the negative of the source 114,
15 current does not flow because the polyaniline remains
insulating. Device 110 is not an exact analogue of a
solid state diode because it is not a two-terminal device
as is a p-n junction or a metal/semiconductor Schottky
barrier. The diode-like behavior of device 110 results
20 from a chemical reaction of the polymer 116 at a
particular potential that causes a change in conductivity
of the polymer 116.

25 Persistent diode-like behavior is obtained by
maintaining one microelectrode, the drain 112, at a

1 negative potential at which it is insulating.
Difficulties are encountered with degradation of the
5 polyaniline when the potential of the microelectrode is
held at a potential positive enough for the polyaniline to
be insulating, +0.7 V vs. SCE, with the other
microelectrode at a more negative potential.

Chemical-based devices depend on chemical
reactions such as redox reactions which occur relatively
slowly compared to the turn on/turn off speeds for solid
10 state diodes and transistors. As shown in Fig. 16, device
110 can be turned on and off in less than one second. In
Fig. 16, the value of I_D is shown for a potential step of
15 V_6 from -0.2 to +0.3 V vs. SCE then back to -0.2 V vs. SCE
at V_D of 0.18 V. By monitoring the rise and fall of I_D of
the potential steps, on to off times of less than 50 ms
and slightly longer off to on times were shown.

The polyaniline-coated device 110 exemplifies
the type of molecule-based devices that could be used as
chemical sensor where the input signal to the device is a
20 redox agent that can equilibrate with the polyaniline 116
to change the value of I_D at a given value of V_D . The
specificity of the device stems from the fact that only
those redox reagents that will bring the electrochemical
25 potential of the polyaniline to a value that will allow
current to pass will be detected. Further specificity

1 arises from the failure of the polyaniline to react with a
particular given redox reagent. For example, polyaniline
does not equilibrate with the H^+/H_2 redox couple. There
is, however, rapid equilibration of polyaniline with one-
5 electron outer-sphere redox reagents such as
 $Ru(NH_3)_6^{3+/2+}$, E^0' approximately equal to -0.18 V vs. SCE
which is close to the E^0' of H^+/H_2 at pH=1 of
approximately -0.3 V vs. SCE.

10 Polyaniline also equilibrates with
 $Fe(CN)_6^{3-/4-}$. For example, immersion of the polyaniline-
based device 110 into a solution of aqueous 0.5 M $NaHSO_4$
containing the oxidant $K_3[Fe(CN)_6]$, E^0' of $[Fe(CN)_6]^{3-/4-}$
approximately equal to +0.2 V vs. SCE, turns the device
"on". Immersion of the device into a solution of 0.5 M
15 $NaHSO_4$ containing $Ru(NH_3)_6^{2+}$ turns the device "off".

20 As depicted in Fig. 17, the change in resistance
of the polyaniline with a change in electrochemical
potential can be brought about by externally connecting
the polyaniline-connected microelectrode array 120 to a
macroscopic indicator electrode 122 that will respond to
reagents 124 other than outer-sphere reagents. When the
indicator electrode 122 is platinum, the microelectrode
array 120 can be equilibrated with H^+/H_2 since platinum
25 equilibrates with H^+/H_2 .

1 The device 130 in Fig. 18 is useful in
characterizing the device of Fig. 17 since the
potentiostat 132 and counter-electrode 134 can be used to
quantitatively establish the amount of charge that is
5 necessary to turn on the device 130. This device differs
from the device 110 shown in Fig. 12a by the presence of
an additional polymer-coated microelectrode and because
the source and drain float.

10 It is also possible to chemically functionalize
the polymer directly, as by the deposition of a metal such
as palladium or a metal oxide onto the polyaniline
connecting the microelectrodes. Palladium provides a
mechanism for equilibrating the polymer with H_2O/H_2 and
 O_2/H_2O .

15 The present invention may be embodied in other
specific forms without departing from the spirit and scope
thereof. These and other modifications of the invention
will occur to those skilled in the art. Such other
embodiments and modifications are intended to fall within
20 the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A device comprising two closely spaced electrically conductive electrodes on an insulating substrate wherein the first electrode is overlaid with a first redox polymer and the second electrode is overlaid with a second redox polymer, wherein the redox potential of said second polymer is different from the redox potential of said first redox polymer.
2. The device of claim 1 wherein said first polymer and said second polymer are not electrically connected.
3. The device of claim 2 wherein said first polymer is reduced and said second polymer is oxidized.
4. The device of claim 3 wherein said device is electrically charged to reduce the first polymer and oxidize the second polymer and wherein said device is useful as an energy storage device.
5. The device of claim 1 wherein said first redox polymer and said second redox polymer are electrically connected by a third polymer, said third polymer reversibly responding to a chemical signal.

6. A triode-like device comprising at least two closely spaced electrodes on an insulating substrate overlaid with an electroactive polymer, wherein said polymer is insulating at a first redox potential, conducting at a second more positive redox potential, and insulating at a third, more positive redox potential.
7. The device of claim 6 wherein said polymer is polyaniline.
8. The device of claim 6 wherein said polymer is responsive to one electron outer-sphere redox reagents.

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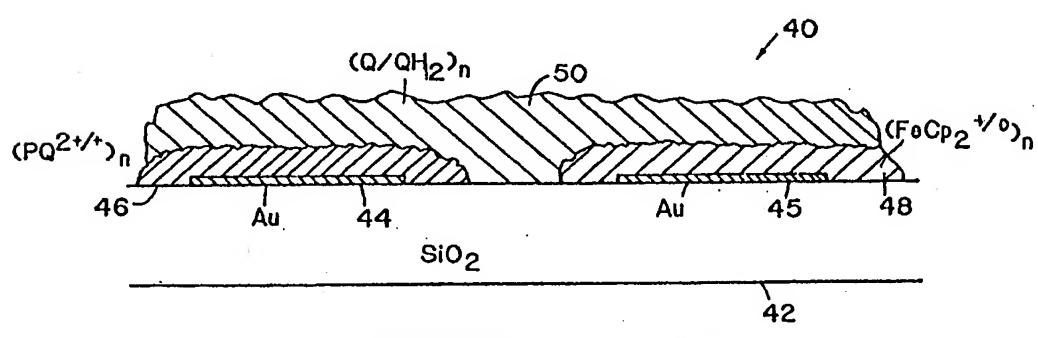
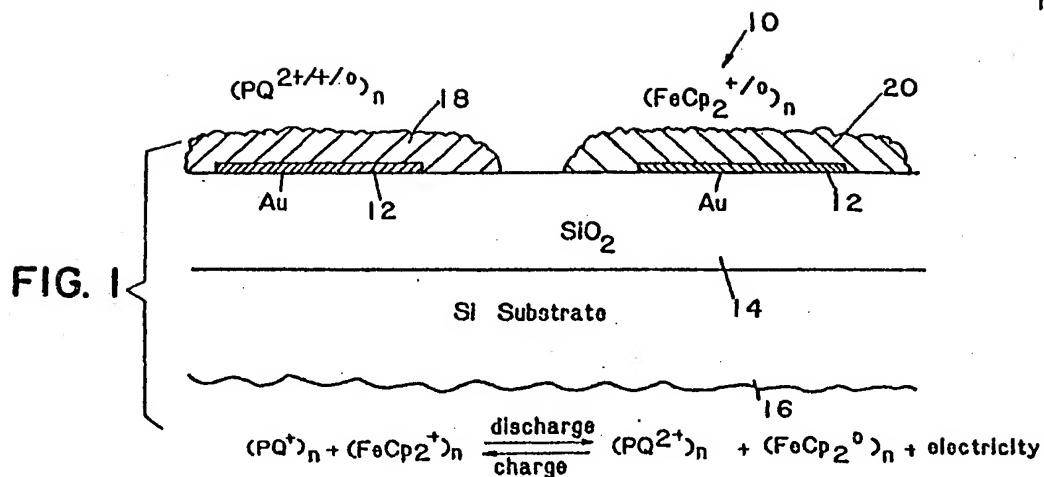
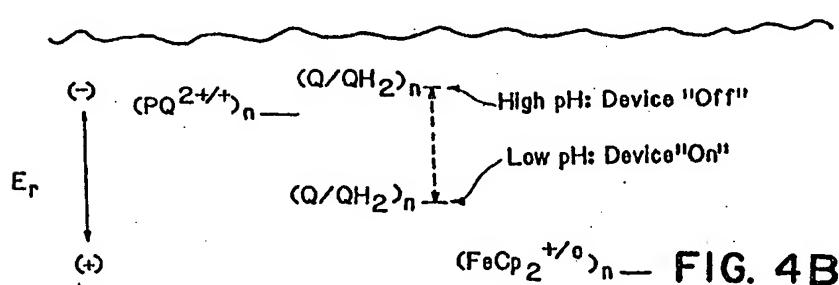


FIG. 4A



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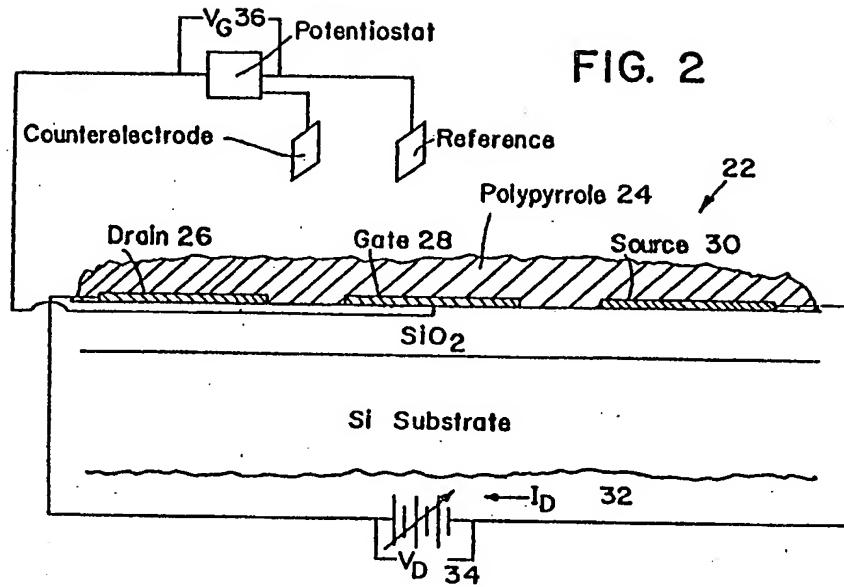
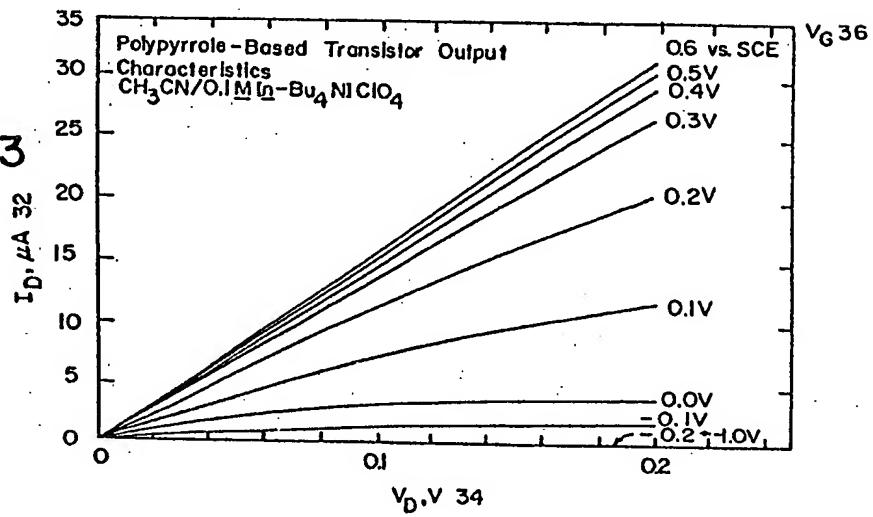


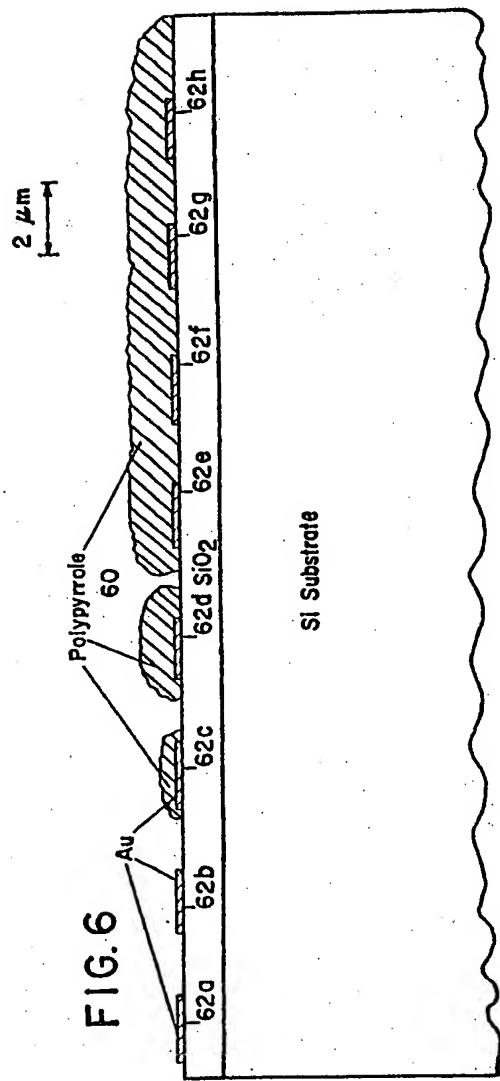
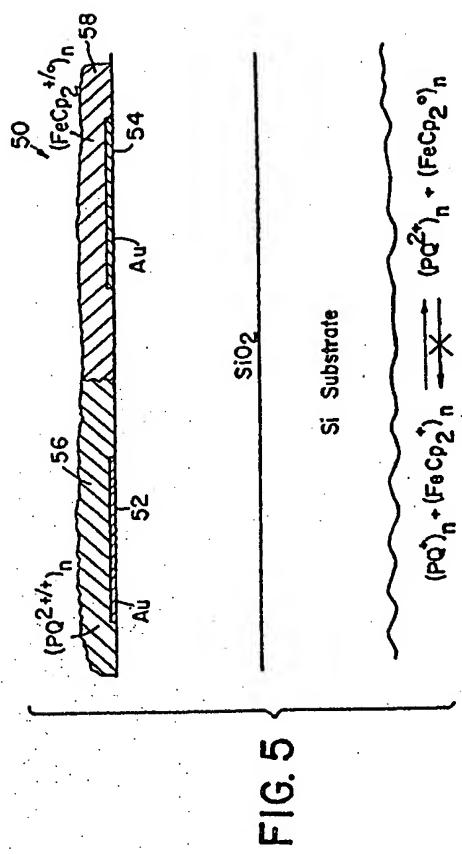
FIG. 3



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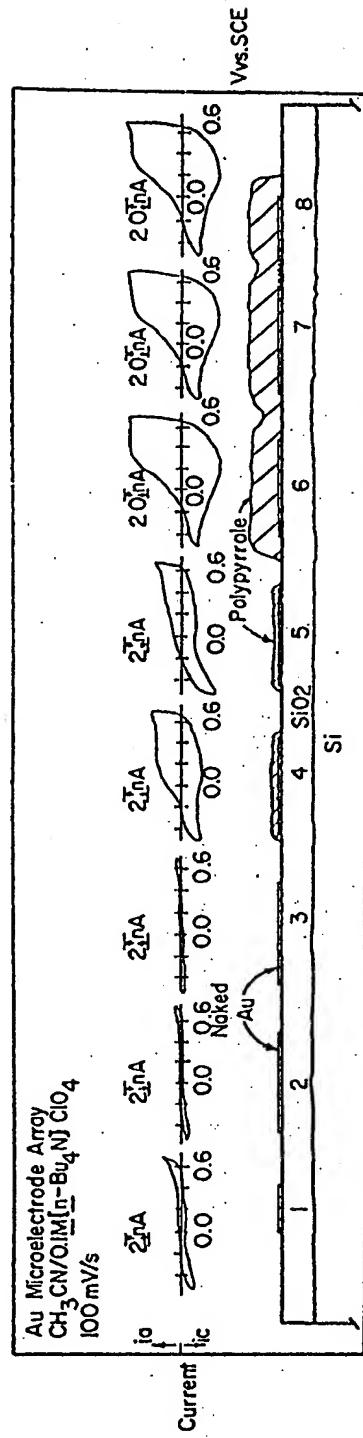
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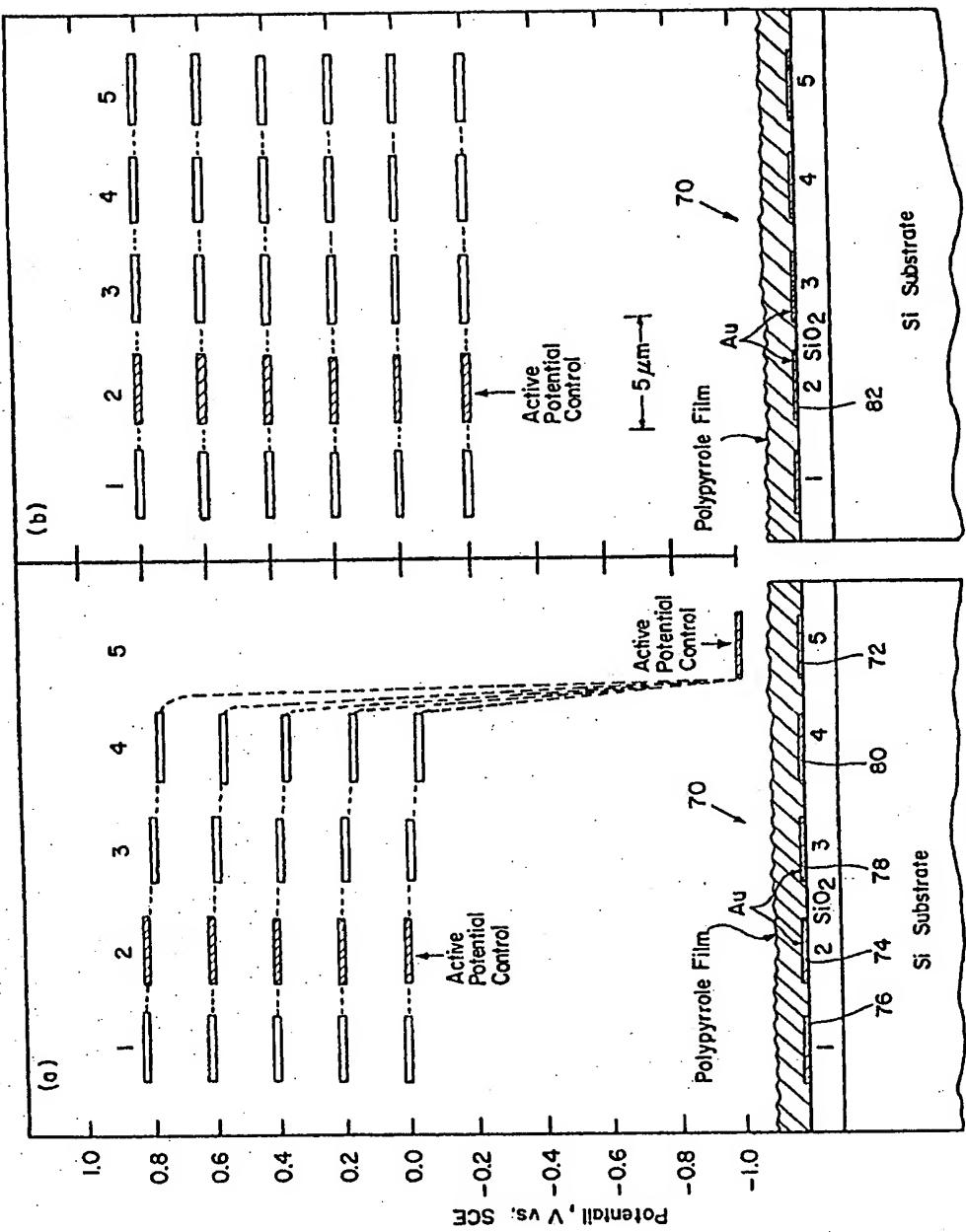


FIG. 8 A

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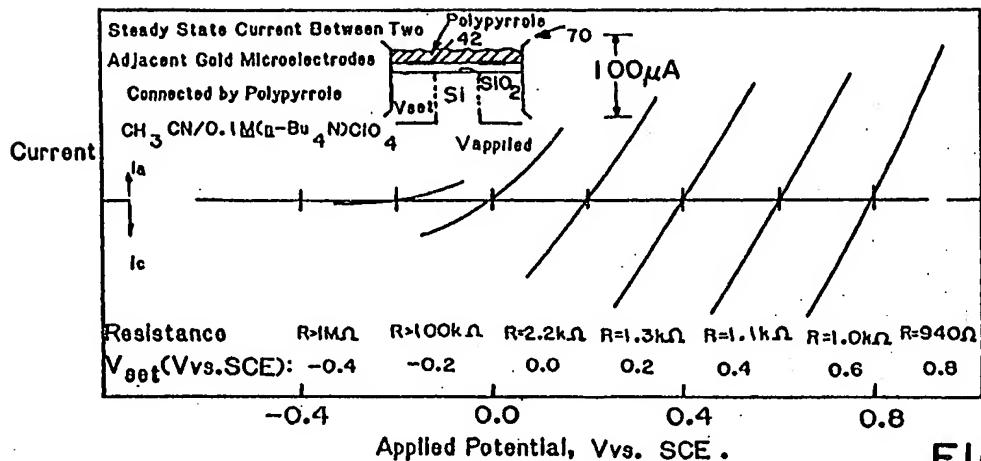


FIG. 9

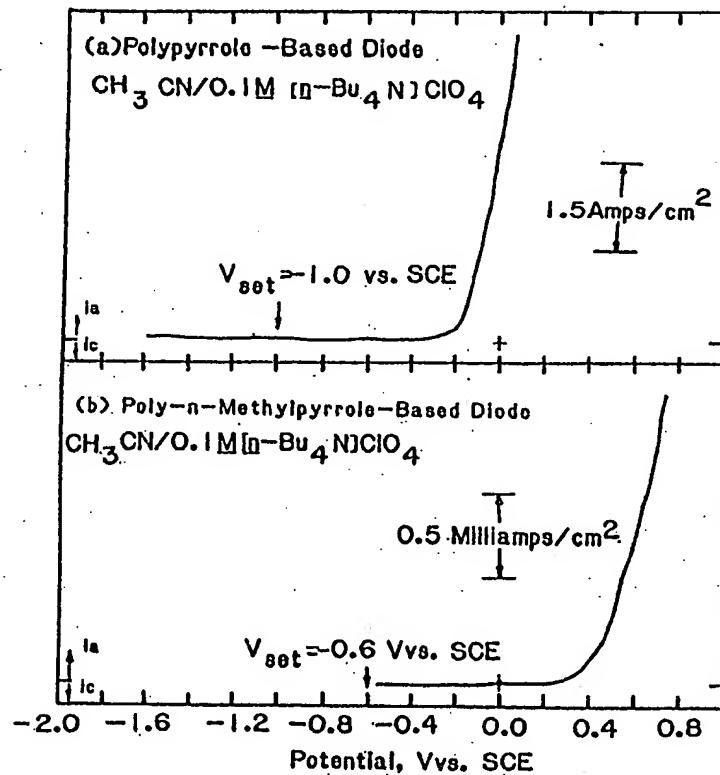


FIG. 10A

FIG. 10B

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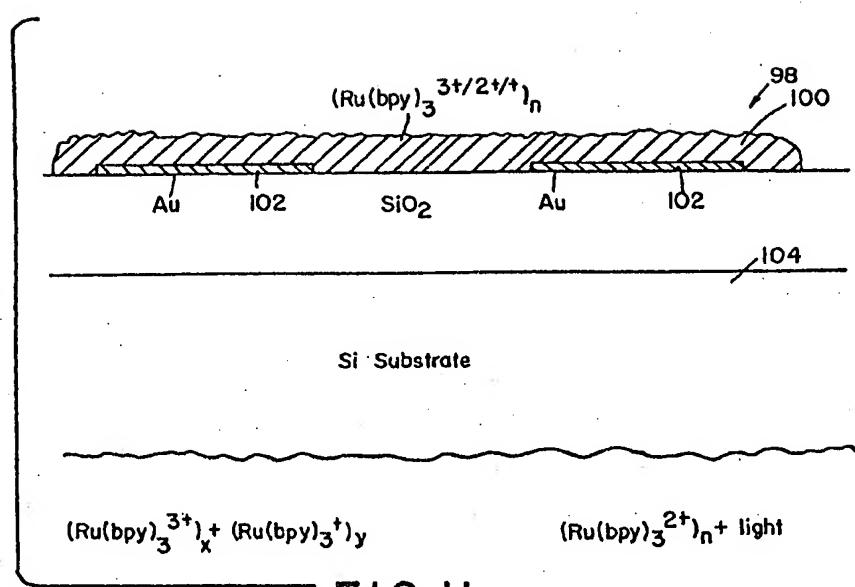


FIG. 11

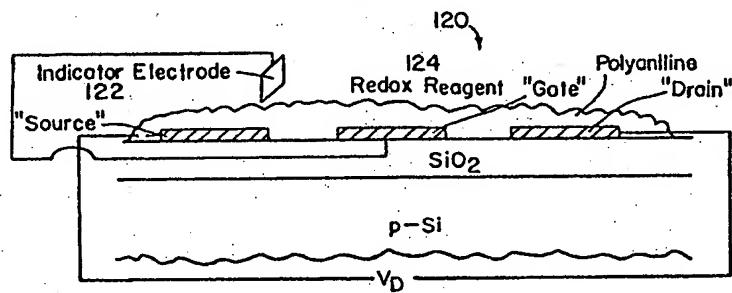


FIG. 17

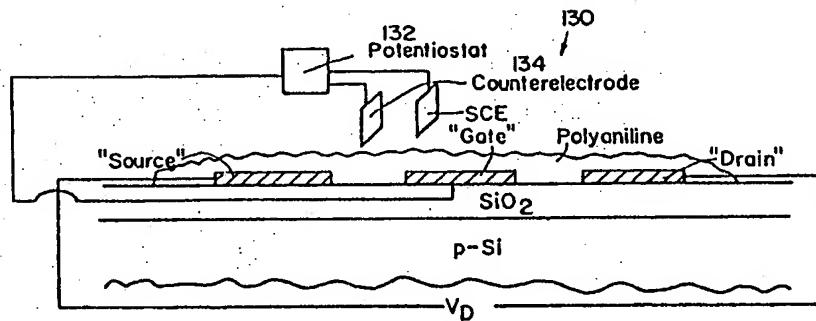


FIG. 18

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FIG. 12B

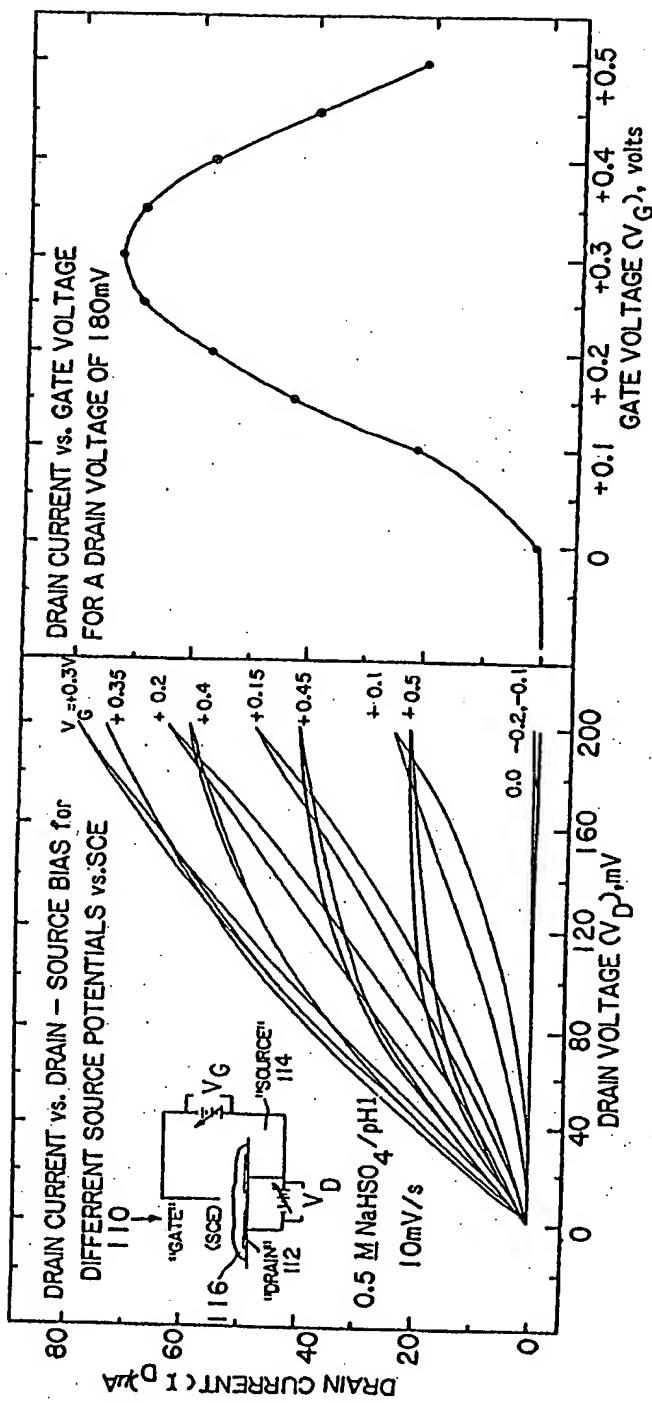


FIG. 12A

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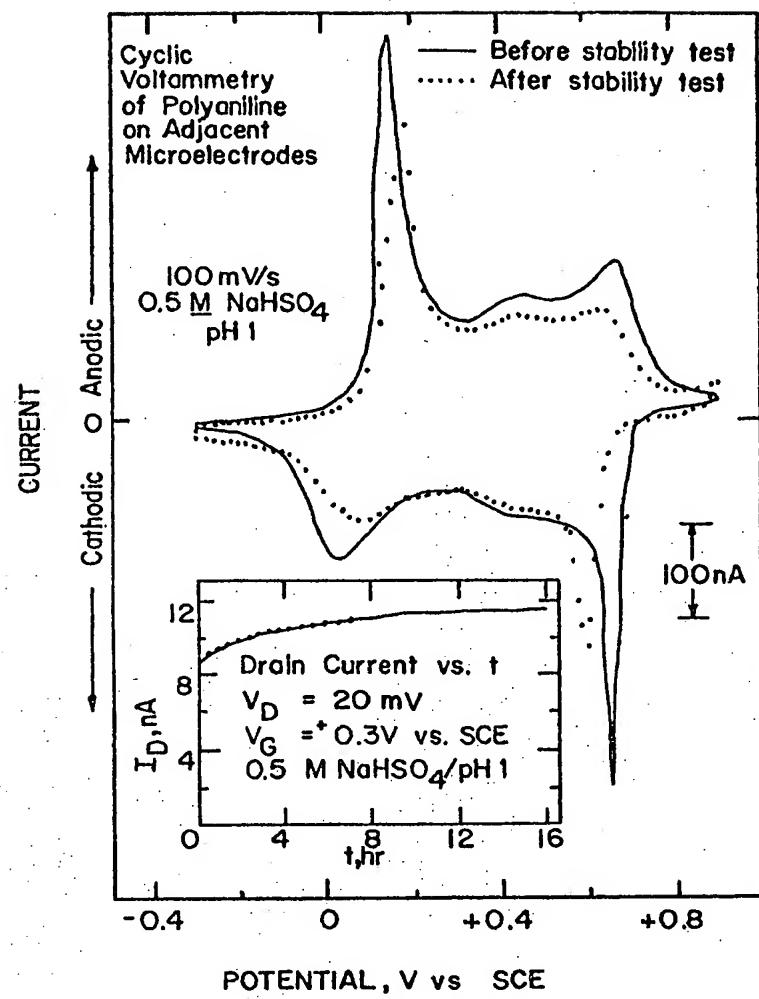


FIG. 13

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FIG. 14A

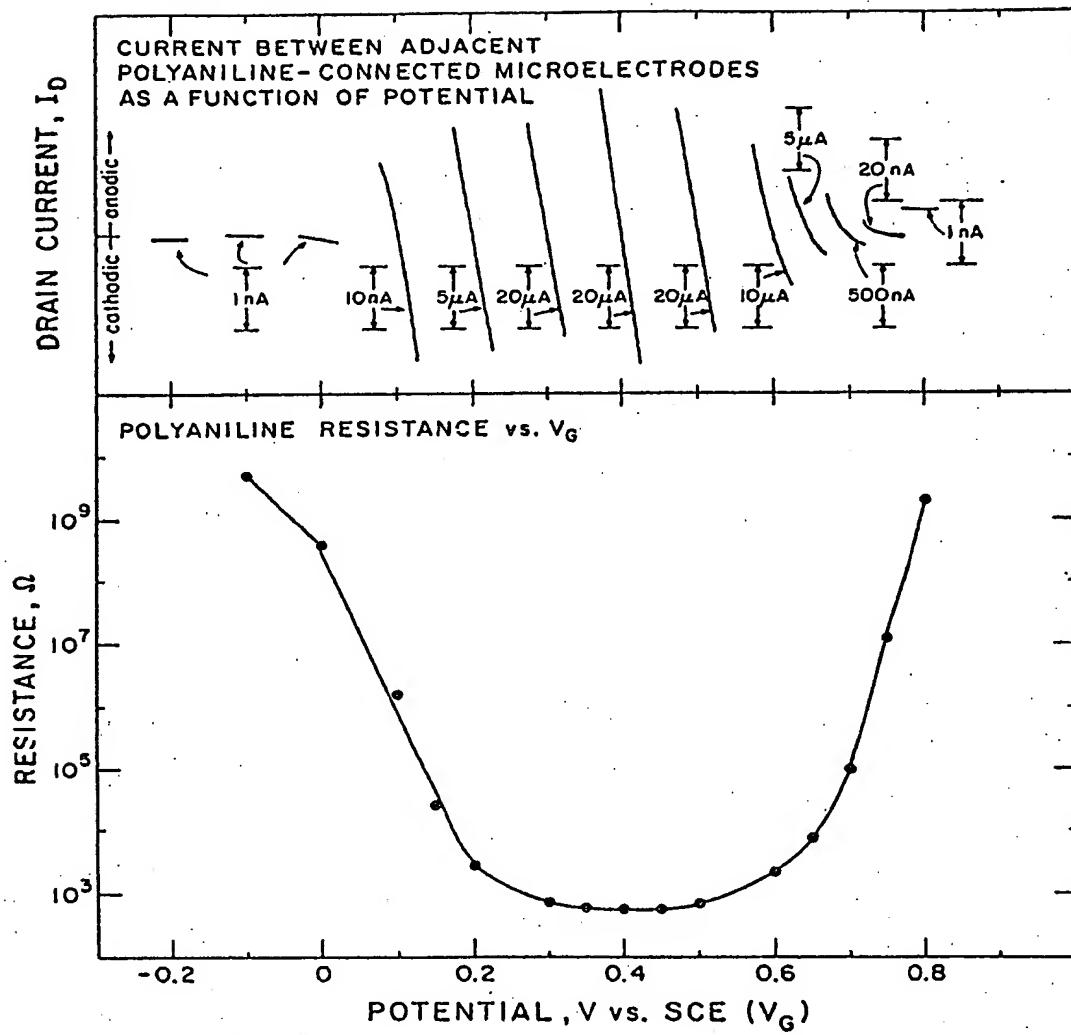


FIG. 14B

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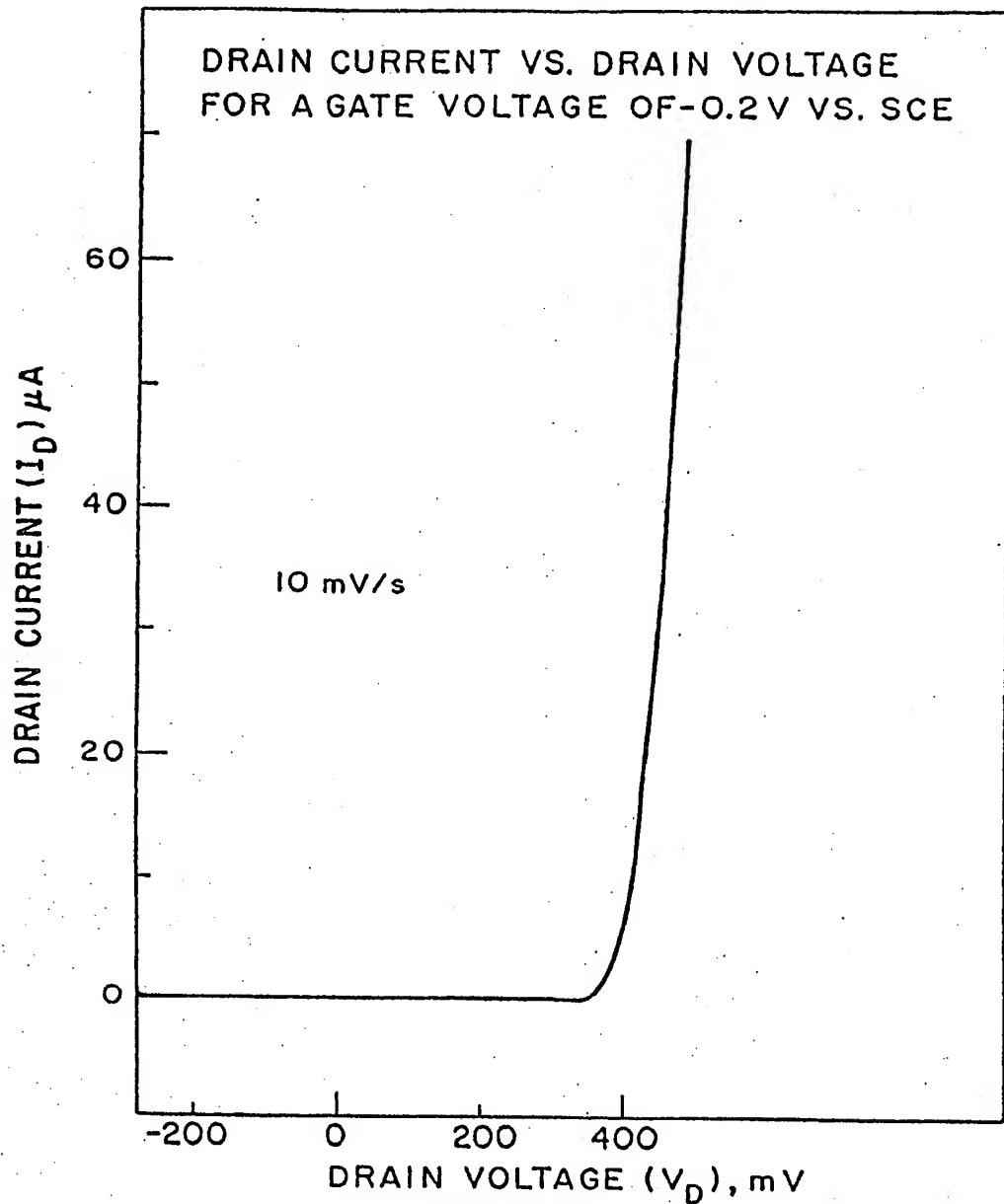


FIG. 15

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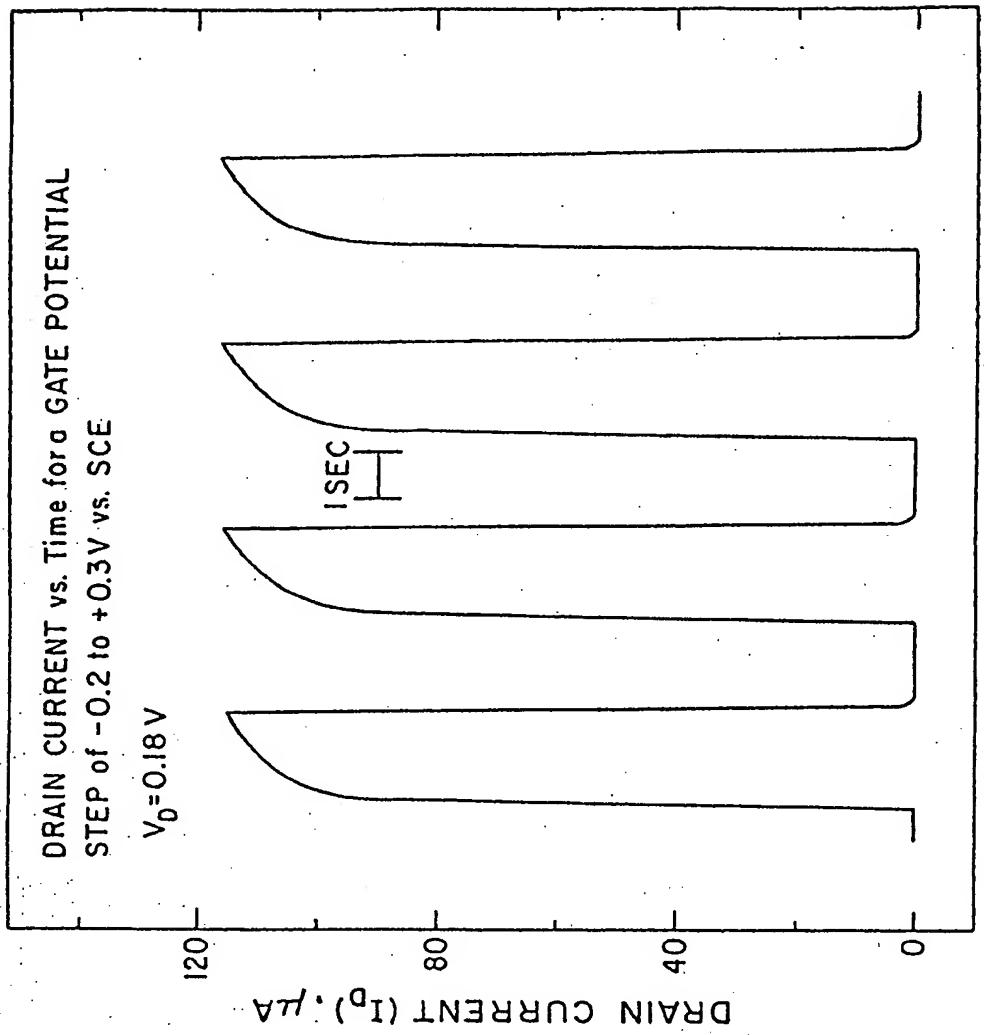


FIG. 16

2. 12-12

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